

liquid. This temperature will be the "hypsometer" point. As these variable factors are operative in any method of boiling a liquid, heating by a flame or by an electric current will give no better results than the method we used. Here again it is necessary to obtain a series of observations and extrapolate to an infinitely small layer of liquid.

In the case of solutions, the hypsometer point cannot be determined directly, so that we must fall back on determinations of the temperatures of the boiling liquid; these are also variable, and it would seem that a definition of what is meant by the boiling point of a solution is required. We would suggest the following:—Assuming that the solution is under a standard atmospheric pressure of 760 mm. of mercury, then the boiling point is the temperature of a small layer when its vapour is in equilibrium with the free vapour above it.

On the Boiling Points of some Saturated Aqueous Solutions.

By THE EARL OF BERKELEY, F.R.S., and M. P. APPLEBY, M.A., B.Sc. (Oxon).

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Introduction and General Discussion.—These experiments were made so as to obtain as accurate data as we could for the purpose of calculating the osmotic pressures of the solutions. The method for determining the boiling points was that already detailed in an earlier communication to the Society,* except that differential platinum thermometers were used as described in the paper "On the Boiling Point of Water."

One of the platinum thermometers was always in the hypsometer, and to get the true boiling point as defined in our previous paper the height of the barometer and height of solution were systematically noted. The chief difficulty of the experiments was that of keeping the solutions saturated. It was found necessary to use a large quantity of finely powdered salt, and to keep the solid in rapid motion by a sufficiently powerful current of steam. If large crystals are used, or if the salt has been left in contact with the solution too long at the end of an experiment, so that crystals have grown, the next experiment will give low values for the equilibrium temperature, showing that the solution is not saturated. At times it happened that a paste of crystals was formed, which offered so much resistance that the

* Berkeley, 'Phil. Trans.,' A, 1904, vol. 203.

steam entered at a pressure greater than normal, thus giving too high a value to the boiling point.

Usually fresh salt was ground up and placed in the apparatus before each determination. The most suitable quantity of salt varies for each substance, but was found by experiment. The rate of passage of steam, as measured in the condenser, was about 3 grm. per minute. The temperature of the solution does not remain constant, but rises continually as the steam condenses, even after saturation is practically reached; this rise is caused by an increase in the height of solution above the orifice, and is quite analogous to the change in boiling point with height of liquid discussed in the preceding paper.

It is evident that the rise due to an increase in depth of liquid will be different for different salts, both because the densities of the saturated solutions are different, and because the solubilities differ, the effect of pressure on the boiling point being greater with the more soluble salts. It was also found that the rate of increase in depth varied with the solubility of the salts.

Particulars of the Salts Used.—Many of the salts were those used in the previous work and recrystallised; these in the following list are marked 1904:—

NaCl. Kahlbaum's purest.

KCl. Merck's "guaranteed."

RbCl. 1904, and a second specimen from Merck which gave higher results, but on the third recrystallisation the results were the same as the 1904.

CsCl. 1904.

TlCl. 1904.

Na₂SO₄. Merck's "guaranteed."

K₂SO₄. Merck's, lower values were obtained after recrystallisation.

Rb₂SO₄. 1904, and some made from Merck's Rb₂CO₃. The whole lot was recrystallised.

Cs₂SO₄. 1904, and some prepared from Merck's Cs₂CO₃. The 1904 sample was accidentally spilled on the bench and contaminated with cyanides; the second contained organic matter. Both were repeatedly recrystallised, and their purity checked by spectroscopic examination.

Tl₂SO₄. 1904.

NaNO₃. Kahlbaum's purest.

KNO₃. Kahlbaum's purest.

CsNO₃. 1904; also used in a research by Mr. T. R. Merton.* This salt was three times recrystallised before use.

SrNO₃. This salt was prepared from the carbonate, and was free from calcium, but it was found to contain a small proportion of barium nitrate. It was freed from the latter salt by dissolving in water and throwing it out of solution by means of alcohol and ether; this process was repeated till no trace of barium could be found on the addition of potassium chromate. It was then repeatedly recrystallised from water. No impurities could be detected in the resulting product.

* 'Journ. Chem. Soc.,' 1910, vol. 97, p. 2454.

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Examples of the Observations.—The following two examples are extracted from the laboratory note-book, and are selected so as to show the difference in behaviour between a very soluble salt such as CsCl and a less soluble one. Each is typical of its class:—

Time.	Corrected barometer.	Level of solution above orifice.	Rate of steam condensed and measured in E.	Corrected balance- point on bridge.	Mean.	Temperature difference from hypsometer.	Remarks.
Experiment with Na ₂ SO ₄ on March 10, 1910. Bridge Extension [2] used (<i>Cf.</i> preceding paper, p. 478).							
A.M.		cm.				° C.	
9.30							Lit up.
10.25	743·7	7·0	20·8 c.c. in 10'	132·70	133·02	2·9334	
10.35				132·96			
10.45				133·03			
11.0	744·3	7·25		133·02			
11.15		7·35		133·02			
11.30				133·20	133·29	2·9372	
11.45	744·3	7·5	133·29				
12.0		7·5	133·29				
12.20			133·39				
12.35		7·85	133·41				
12.50	744·3	7·95		133·47	133·42	2·9391	
Experiment with CsCl on October 9, 1910. Bridge Extensions [2] and [16] used.							
9.30							Lit up.
10.5	751·3		30·0 c.c. in 10'				
10.20		2·5		91·5			
10.30	751·2	2·75		93·73			
10.35	751·2	2·9		95·09	95·09	19·879*	
10.45	Found all the salt dissolved and the temperature falling rapidly; added more salt						
11.0	751·2	3·7		95·60			
11.5				95·56			Temp. falling, added salt.
11.25	751·2	4·8		96·12			
11.30		4·9		96·53			
11.35	751·2	5·1		97·27	97·26	19·912*	Added salt.
11.40		5·1		97·25			
11.55	751·1	6·4	30·0 c.c. in 10'	98·24			
12.0		6·55		98·79	98·91	19·936*	
12.5		6·7		98·89			
12.10	751·0	6·8		99·06			
12.25		7·2		100·13	100·26	19·957*	
12.35	751·0	7·4		100·39			

It should be mentioned that the numbers given under the heading "corrected balance-point on bridge" are the null points calculated from the observed deflections when the contact was 1 mm. above and 1 mm. below the null point, both readings being repeated with the current reversed. This value is then corrected for errors in the bridge wire and for slight inequalities in the proportional arms.

The numbers marked with an * are derived from the "means" by correcting the latter to a constant barometer pressure of 750 mm., by the aid of a "barometer coefficient" = 0·00608° C. = 0·42 bridge mm. per millimetre of mercury. This barometer coefficient is discussed below.

The Barometer Coefficients.—The effect of changes in barometric pressure on the temperature equilibrium is greater in the case of saturated solutions than with water. This is in part due to changes of solubility with pressure, and results, to a certain degree, in making the differential arrangement of the platinum thermometers not so effective in eliminating the variations in barometric height.

We have therefore arranged the observations (by determining boiling points at differing barometric pressures) so that a barometer coefficient may be calculated for each salt; in every case the coefficient is derived from the mean of two or more determinations, and it represents the excess of the effect on the temperature of the boiling saturated solution produced by a rise of barometer of 1 mm. over the corresponding effect on the temperature of the steam in the hypsometer.

The magnitude of the coefficient depends upon the solubility of the salt and also on the temperature coefficient of solubility; thus for Na_2SO_4 , which is only moderately soluble and does not vary in solubility with temperature, the coefficient is only 0.00052°C. , while for KNO_3 , which has both a high solubility and a large temperature coefficient of solubility, the coefficient is 0.0217°C.

The barometer readings given in the tables were obtained thus:—Before an experiment, the standard barometer (it was standardised at Kew) was compared with a Callendar sulphuric acid barometer of a large size; the latter had been adjusted successfully so as to have practically no temperature coefficient (its sensitiveness was such that 1 mm. change in the mercury barometer caused a change in it of 2.05 mm.), and all readings during the experiment were taken on the Callendar instrument.

Results of the Observations.—The following tables give the results of the observations. It was found that variations in the rate of passage of steam make but little difference to the extrapolated (see later) “equilibrium” temperature for zero height of liquid, so that these rates are not tabulated but two sets of observations are given for TiCl and for Cs_2SO_4 to show the effect. The last column of figures in each table gives the rise in temperature above the hypsometer for a constant barometric pressure which is somewhere near the mean of the various pressures noted in the second column; these numbers are calculated by means of the barometer coefficient given at the head of the table:—

Table I.

Height above orifice.	Corrected barometer.	Observed rise in temperature above hypsometer.	Corrected rise.
NaCl. (Bar. coeff. = 0.00103° per mm. Hg.)			
cm.	mm.	° C.	° C.
2.35	745.4	8.6809	8.6805 Corrected to 745 mm. Hg.
3.47	744.0	.6942	.6952 " "
3.8	733.4	.6894	.7013 " "
4.3	741.0	.7069	.7110 " "
[4.8	723.9	.7077	.7294]* " "
4.85	729.0	.7021	.7186 " "
5.0	744.4	.7189	.7195 " "
7.0	751.1	.7573	.7510 " "
* A single unconfirmed determination.			
KCl. (Bar. coeff. = 0.00242° per mm. Hg.)			
3.55	746.5	8.5868	8.5953 Corrected to 750 mm. Hg.
4.55	744.6	.5915	.6046 " "
5.05	758.8	.6350	.6137 " "
5.15	756.5	.6231	.6067 " "
5.5	746.9	.6011	.6086 " "
5.5	748.6	.6039	.6073 " "
8.45	744.4	.6340	.6476 " "
RbCl. (Bar. coeff. = 0.0021° per mm. Hg.)			
1904 salt—			
3.07	750.6	13.7090	13.7078 Corrected to 750 mm. Hg.
4.1	750.2	.7200	.7196 " "
4.85	752.3	.7332	.7284 " "
5.4	750.2	.7424	.7420 " "
7.05	751.7	.7707	.7671 " "
Impure—			
2.8	747.4	.7304	.7359 " "
4.0	747.8	.7514	.7560 " "
4.8	750.0	.7603	.7603 " "
5.6	749.3	.7688	.7705 " "
1st recrystallisa- tion—			
2.55	747.9	.7086	.7130 " "
3.5	746.9	.7228	.7293 " "
2nd recrystallisa- tion—			
2.4	753.2	.7135	.7068 " "
4.35	747.1	.7202	.7263 " "
5.8	747.6	.7430	.7480 " "
CaCl. (Bar. coeff. = 0.00608° per mm. Hg.)			
2.4	750.8	19.8842	19.8793 Corrected to 750 mm. Hg.
3.2	750.8	.8917	.8868 " "
3.6	744.6	.8613	.8941 " "
4.6	750.8	.9162	.9113 " "
6.2	750.6	.9405	.9369 " "
6.9	750.6	.9606	.9570 " "

Table I—*continued*.

Height above orifice.	Corrected barometer.	Observed rise in temperature above hypsometer.	Corrected rise.
TiCl. (Bar. coeff. = 0.00029° per mm. Hg.)			
cm.	mm.	° C.	° C.
2.9	751.3	0.0996	0.1000 Corrected to 750 mm. Hg.
3.0	735.7	.0964	.1005 " "
3.0	752.5	.1004	.0997 " "
3.15	748.5	.1004	.1008 " "
3.3	737.4	.0971	.1008 " "
3.55	742.2	.0996	.1019 " "
3.8	750.5	.1054	.1053 " "
3.8	743.3	.1030	.1049 " "
4.0	746.3	.1040	.1051 " "
4.8	748.0	.1077	.1083 " "
4.95	757.0	.1125	.1105 " "
5.1	749.5	.1117	.1118 " "
5.5	748.0	.1146	.1152 " "
7.0	748.4	.1310	.1315 " "
Another set with a higher rate of steam.			
2.4	728.9	0.0971	0.0974 Corrected to 730 mm. Hg.
2.9	729.4	.1005	.1007 " "
3.4	730.0	.1043	.1043 " "
4.3	730.4	.1084	.1083 " "
5.2	734.1	.1136	.1124 " "
5.25	732.2	.1136	.1130 " "
7.0	727.2	.1284	.1292 " "
7.1	731.9	.1295	.1289 " "
Na ₂ SO ₄ . (Bar. coeff. = 0.00052° per mm. Hg.)			
3.77	742.2	2.9031	2.9046 Corrected to 745 mm. Hg.
4.15	749.45	.9100	.9077 " "
4.35	749.45	.9124	.9101 " "
4.95	744.4	.9164	.9167 " "
5.1	743.95	.9185	.9190 " "
5.7	740.35	.9203	.9227 " "
5.75	742.4	.9228	.9242 " "
6.75	743.85	.9335	.9341 " "
7.0	743.85	.9374	.9380 " "
7.3	742.7	.9418	.9430 " "
K ₂ SO ₄ . (Bar. coeff. = 0.00014° per mm. Hg.)			
2.3	763.2	1.3967	1.3963 Corrected to 760 mm. Hg.
3.6	763.6	.4027	.4022 " "
4.05	750.1	.4044	.4058 " "
4.3	750.1	.4063	.4077 " "
5.8	762.9	.4210	.4206 " "
6.85	763.2	.4365	.4361 " "
Rb ₂ SO ₄ . (Bar. coeff. = 0.00043° per mm. Hg.)			
4.5	746.3	3.5373	3.5389 Corrected to 750 mm. Hg.
4.5	754.0	.5395	.5378 " "
5.45	745.8	.5465	.5483 " "
5.6	745.8	.5491	.5509 " "
5.95	754.0	.5577	.5560 " "
6.2	754.0	.5621	.5604 " "
7.1	755.0	.5751	.5730 " "

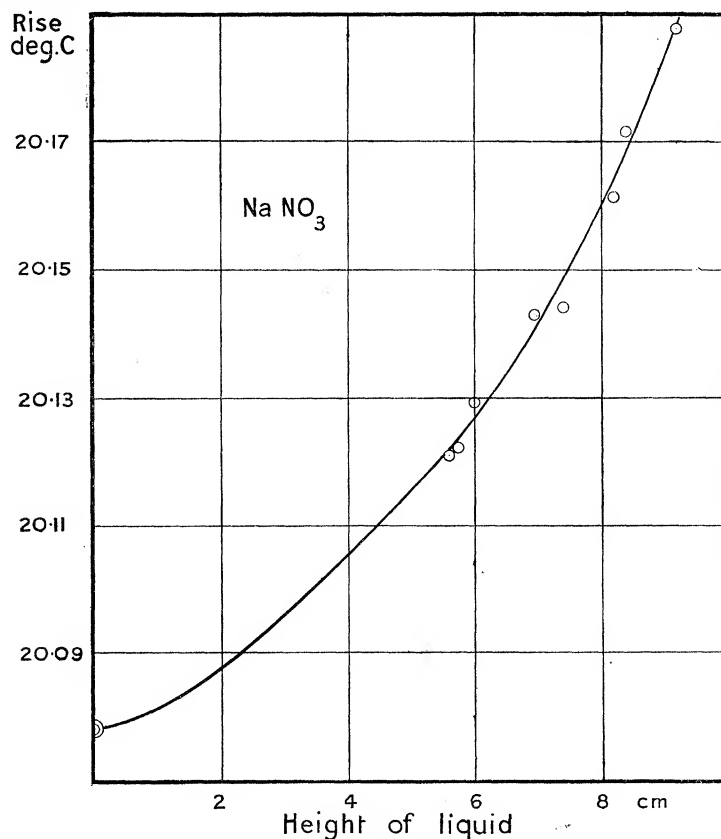
Table I—continued.

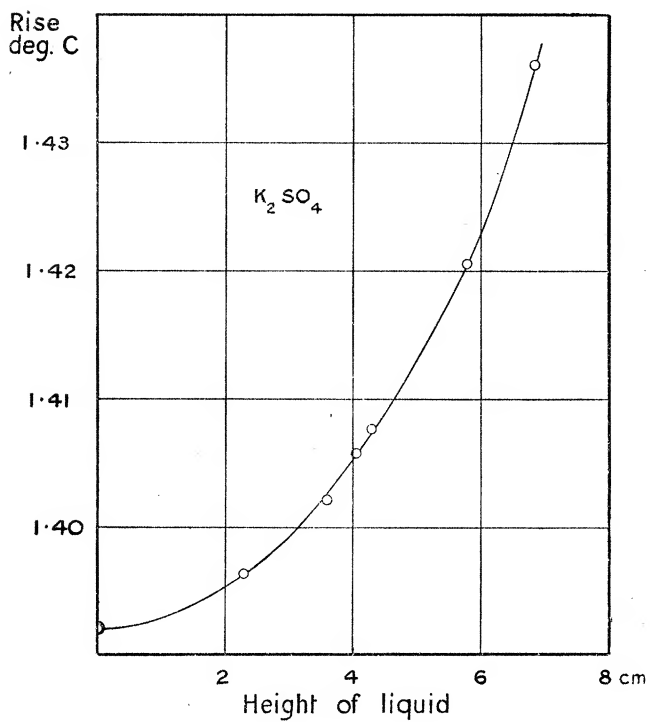
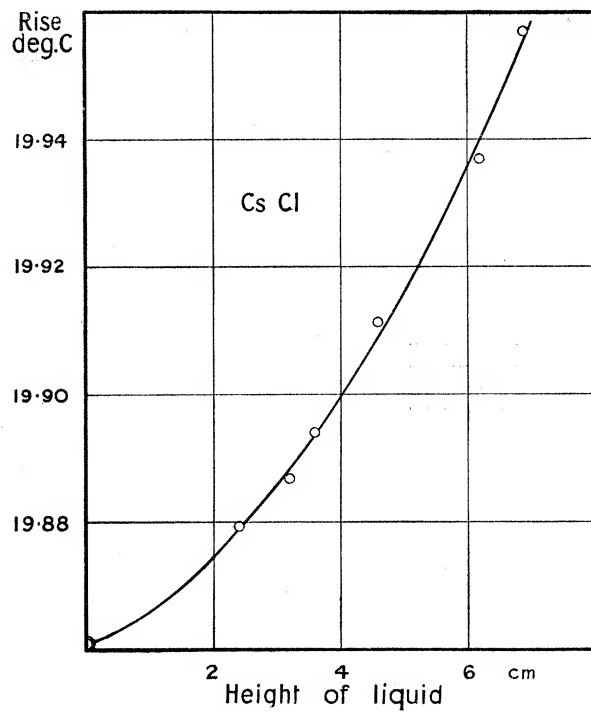
Height above orifice.	Corrected barometer.	Observed rise in temperature above hypsometer.	Corrected rise.
Cs₂SO₄. (Bar. coeff. = 0.00100° per mm. Hg.)			
cm.	mm.	° C.	° C.
2.55	750.4	9.9701	9.9697 Corrected to 750 mm. Hg.
3.2	750.4	.9774	.9770 " "
4.58	747.5	.9852	.9877 " "
4.95	755.7	10.0063	10.0006 " "
5.1	747.6	9.9954	9.9978 " "
5.3	747.5	10.0024	10.0049 " "
6.2	747.5	.0244	.0269 " "
6.25	755.5	.0304	.0249 " "
Another set with a higher rate of steam.			
2.2	749.4	9.9714	9.9720 Corrected to 750 mm. Hg.
2.7	744.5	.9729	.9784 " "
3.62	745.3	.9852	.9899 " "
3.65	751.3	.9899	.9886 " "
3.75	756.2	.9974	.9912 " "
4.4	755.7	10.0057	10.0000 " "
5.1	749.9	.0181	.0182 " "
Tl₂SO₄. (Bar coeff. = 0.00022° per mm. Hg.)			
4.3	746.5	0.3293	0.3301 Corrected to 750 mm. Hg.
4.75	742.9	.3317	.3333 " "
5.1	748.8	.3352	.3355 " "
5.7	739.7	.3367	.3390 " "
5.9	752.1	.3427	.3422 " "
6.1	752.5	.3446	.3440 " "
6.3	752.3	.3472	.3467 " "
NaNO₃. (Bar. coeff. = 0.00835° per mm. Hg.)			
5.6	743.7	20.1102	20.1211 Corrected to 745 mm. Hg.
5.75	738.4	.0671	.1222 " "
6.0	743.8	.0195	.1295 " "
6.95	745.9	.1506	.1431 " "
7.4	751.7	.2001	.1442 " "
8.2	745.8	.1681	.1614 " "
8.4	751.3	.2242	.1716 " "
9.2	739.9	.1452	.1878 " "
KNO₃. (Bar. coeff. = 0.0217° per mm. Hg.)			
2.5	746.1	15.2950	15.3796 Corrected to 750 mm. Hg.
3.6	747.9	.3614	.4070 " "
3.7	750.5	.4224	.4116 " "
5.4	750.0	.4596	.4596 " "
7.2	746.2	.4161	.4986 " "
9.8	746.3	.4900	.5703 " "
CsNO₃. (Bar. coeff. = 0.0044° per mm. Hg.)			
3.6	753.1	7.2193	7.2057 Corrected to 750 mm. Hg.
4.05	751.5	.2182	.2116 " "
4.2	751.4	.2163	.2111 " "
4.6	751.4	.2312	.2250 " "
5.3	751.4	.2397	.2335 " "
5.7	751.4	.2483	.2421 " "
7.3	751.0	.2974	.2930 " "

Table I—*continued*.

Height above orifice.	Corrected barometer.	Observed rise in temperature above hypsometer.	Corrected rise.
Sr(NO₃)₂. (Bar. coeff. = 0·00200° per mm. Hg.)			
cm.	mm.	° C.	° C.
3·9	735·7	6·7577	6·7663 Corrected to 740 mm. Hg.
4·05	741·1	·7714	·7692 " "
5·3	739·6	·7785	·7793 " "
5·45	735·7	·7737	·7823 " "
7·45	735·7	·7996	·8082 " "
Cæsium alum. (Bar. coeff. = 0·00115° per mm. Hg.)			
2·5	745·8	0·5191	0·5182 Corrected to 745 mm. Hg.
3·7	735·3	·5121	·5232 " "
3·8	745·8	·5248	·5239 " "
5·0	745·9	·5347	·5337 " "
5·1	745·9	·5362	·5352 " "
6·1	745·9	·5458	·5448 " "

We give some curves, where the corrected rise is plotted against height, for three salts of widely different solubilities; these may be taken as types for the others.





The following table gives a comparison between Buchanan's* barometer coefficients and ours for the salts we both have worked with:—

Table II.

Salt.	Barometer coefficient.	
	Buchanan's.	B. and A.'s.
	° C.	° C.
NaCl	0·0018	0·00103
KCl	0·0032	0·00242
NaNO ₃	0·0128*	0·00835
K ₂ SO ₄	0·00087	0·00014

* All Buchanan's observations on NaNO₃ were made with the barometer below 620 mm.

Theory.—In the case of water, where the curve connecting the equilibrium temperature with the height of liquid is known to cut the temperature axis at the hypsometer point, we were able to derive an equation, from theoretical considerations, which fitted the observations. This equation shows the curve to be a hyperbola.

In conformity with the definition previously given of the boiling point of a solution, it is required, in the present case, to obtain a means of correctly extrapolating to the equilibrium temperature at zero height of liquid.

On plotting the numbers under the heading "corrected rise" against the height of solution (see typical curves on pp. 496–7), it is at once apparent that, as for water, the graphs are not straight lines, but are convex to the axis along which the depth of solution is measured. The obvious similarity between the water and solution curves suggests that the latter are also hyperbolas.

If, on the one hand, we extrapolate to zero height by means of a bent steel ruler, and on the other we calculate the same point on the assumption that a hyperbola fits the observations, we get the numbers given in Table III.

It is evident that a considerable divergence exists between the two methods of extrapolating; in most cases the difference is greater than the experimental error.

The theoretical formulæ developed in the preceding paper are applicable in their entirety to the saturated solutions—for although the conditions of the experiments here considered differ in some respects from those pertaining to water, they, as will be shown, scarcely affect the argument.

* Buchanan, 'Trans. Roy. Soc. Edin.,' 1899, vol. 39, p. 529.

The principal differences are detailed in paragraphs (a), (b), (c), and (d) below.

(a) There is no question but that the liquid is now entirely heated by the condensation of steam; for in most cases the temperature of the entering steam is less than that of the solution, and the latter is only heated because its vapour-pressure is less than the steam pressure.

Table III.

Substance.	Barometer.	Rise by steel ruler.*	Calculated rise.
	mm.	° C.	° C.
NaCl	745	8·640	8·653
KCl	750	8·567	8·576
RbCl	750	13·682	13·689
CsCl	750	19·861	19·861
TlCl	750	0·091	0·094
„	730	0·086	0·090
Na ₂ SO ₄	745	2·880	2·877
K ₂ SO ₄	760	1·387	1·392
Rb ₂ SO ₄	750	3·502	3·506
Cs ₂ SO ₄	750	9·953	9·953
„	750	9·955	9·955
Tl ₂ SO ₄	750	0·312	0·315
NaNO ₃	745	20·037	20·078
KNO ₃	750	15·310	15·332
CsNO ₃	750	7·163	7·184
Sr(NO ₃) ₂	740	6·742	6·750
Cæsium alum	745	0·506	0·511

* This extrapolation was done separately by two unbiassed observers, and the numbers tabulated are the mean of their results.

(b) The possible cooling effect taking place through the walls of the boiling vessel; this, in the case of high boiling points, might at first sight be thought to cause a considerable loss of heat, but when it is remembered that the walls of the outer vessel are thoroughly lagged, it can be safely assumed that most of the heat lost by the solution in this way is returned to it by the extra heat imparted to the entering steam, so that the balance is scarcely disturbed.

(c) The rate of increase in the depth of some of the solutions was much faster than in the case of water, in fact it was as much as 3 mm. in 10 minutes (the quantity of steam passing through the solution in the same time was 30 grm.); this phenomenon prevented us from reaching a true equilibrium. The results, however, are unaffected, for the depth of solution was always measured shortly before and after the temperature was determined, and these numbers were used for the curve.

It should be mentioned that a momentary maximum temperature can always be reached, but this maximum is not the true boiling point of the

saturated solution; it can be realised easily that the maximum only shows when the quantity of salt left in the liquid is not enough to keep it saturated; this, indeed, was quite apparent to the eye. No temperatures here recorded are other than those that we are satisfied belong to solutions which were saturated at the time of observation.

(*d*) The mean area of a bubble may still be taken as constant; for even supposing that the whole change of level in the solution were caused by steam condensed out of the bubbles as they rise, the consequent change in area will only be small. Thus, taking the most rapid rise of all (caesium chloride), where the level changed by a height equivalent to 3 c.c. in 10 minutes, while the amount of steam condensed in the condenser was 30 grm., the consequent volume change in the bubbles is only about 9 per cent., and the area change 5 per cent. This quantity may be neglected in view of the fact that the rise of level is largely caused by steam condensing (and running back into the solution) on the exposed walls of the boiling vessel, which may be taken to be covered by a relatively cold film of solution thrown there by the breaking bubbles. That this explanation is correct is shown by the fact that, with all the salts, the depth of liquid had no appreciable influence on the rate at which the level rose; in other words, the rise is approximately independent of the number of steam bubbles in contact with the liquid.

Final Results for the Boiling Points.—In view of the previous discussion, it may be assumed that the curve of boiling point plotted against height of liquid is a hyperbola.

On this assumption we have extrapolated to a height $h = 0$, by two methods, one by calculation from equation (2) of the previous paper, and the other by a very convenient method suggested to us by Mr. A. F. Pedder, of Magdalen College (Oxford).—See Appendix II.

For the first method we passed a smooth curve through the experimental points, and using this curve to obtain the constants of the equation, we deduced a value for t when $dt/dh = 0$; in the second method, which is applicable to any hyperbola (not necessarily one which cuts the axis of temperatures at right angles), we extrapolated from the actual experimental points to the point where the curve cuts the temperature axis.

The greatest divergence between the results of the two methods was 0.016° C. for sodium nitrate, where the experiments, owing to the high solubility, were somewhat inaccurate. Except for this discrepancy, the deviation was never greater than 0.01° , and was usually much less.

We would lay considerable emphasis on this fact; for it seems to be confirmatory evidence for the validity of the various assumptions that we

have made during the theoretical discussion both in this communication and in that on the boiling point of water.

The means of the two methods of extrapolating are given in the following table and are the final results for $h = 0$. The second column gives the

Table IV.

Substance.	Barometer.	Boiling point under pressure in second column.	Boiling point under standard conditions.	Buchanan's boiling points extrapolated to 760 mm.
	mm.	° C.	° C.	° C.
NaCl	745	108·096	108·668	108·50
KCl	750	108·205	108·599	108·35
RbCl	750	113·318	113·710	
CsCl	750	119·488	119·919	
TlCl	750	99·724	100·097	
„	730	98·967	100·099 (100·098)	
Na ₂ SO ₄	745	102·320	102·885	
K ₂ SO ₄	760		101·392	101·41
Rb ₂ SO ₄	750	103·136	103·511	
Cs ₂ SO ₄	750	109·583	109·963	
„	750	109·585	109·965 (109·964)	
Tl ₂ SO ₄	750	99·945	100·317	
NaNO ₃	745	119·514	120·20	118·71
KNO ₃	750	114·962	115·549	
CsNO ₃	750	106·814	107·228	
Sr(NO ₃) ₂	740	106·005	106·790	106·52
Cæsium alum ...	745	99·954	100·527	

height of the barometer to which the boiling points given in the third column have been corrected, while the fourth column gives the boiling points corrected to 760 mm. pressure and to sea level and latitude 45°. The fifth column gives Buchanan's values extrapolated to a barometer pressure of 760 mm.

Experimental Error.—In view of the close agreement shown to obtain in the two methods of extrapolation, and also in the two sets of observations for TlCl and Cs₂SO₄ we think we may say that the final boiling points probably do not differ from the truth by more than 0·005° C.; this involves all errors in the barometer coefficients, but the actually observed boiling points for the same height and rate of bubbling agree more closely.

The Osmotic Pressures.—One of us pointed out in a letter to 'Nature'* that osmotic pressures derived from vapour-pressure observations can be measured in two ways—one, with the pressure on the solvent constant, and the other with the constant pressure on the solution; in the former case, as can be seen from Prof. Porter's fundamental equation,† it is necessary to determine the space occupied by the solvent in the solution, and this involves a series of

* 'Nature,' 1906, vol. 74, p. 7.

† 'Roy. Soc. Proc.,' A, 1907, vol. 79, p. 521.

measurements of the compressibilities together with the densities of the solutions.

Prof. Porter's fundamental equation, for the case where the pressure on the solution is its own vapour pressure, becomes*

$$\int_{\pi_{\pi}-P_{\pi}}^{\pi_{00}} u dp = \int_{\pi_{\pi}}^{\pi_{00}} v dp, \quad (1)$$

where π_{00} is the vapour-pressure of the solvent when under the hydrostatic pressure of its own vapour, π_{π} is the vapour-pressure of the solution, v is the specific volume of the vapour, u is the specific volume of the pure solvent, p is the hydrostatic pressure, and P_{π} is the osmotic pressure when the solution is under the hydrostatic pressure of its own vapour. This equation, neglecting the pressure effect of the slightly different vapour-pressures of different solutions, enables us to bring the calculated osmotic pressures of solutions of different solutes (in the same solvent) into direct comparison. It, however, involves (as the u term shows) a knowledge of the specific volume and compressibility of the pure solvent when under a negative pressure.

Equation (1) reduces to

$$P = \pi_{00} v \log_e \pi_{00} / \bar{u} - \pi_{00} + \pi_{\pi},$$

where $\bar{u}$ is the mean value of the specific volume of water between the limits in the integral; this value, in the calculations, has been obtained by extrapolating to negative pressures the known compressibility of water.

The results of the calculations are given in the following table:—

Table V.

Salt.	Boiling point.	$\bar{u}$.	Osmotic pressure.	No. of grm. mols. per litre of solution.	Osmotic pressure Grm. mols. per litre.
			atmos.		
NaCl	108·668	1·0628	476·8	5·648	84·4
KCl	108·599	1·0627	473·3	5·985	79·1
RbCl	113·510	1·0742	743·2	7·948	93·5
CsCl	119·919	1·0883	1055·0	9·214	114·5
TlCl	100·097	1·0443	5·5	0·097	57·0
Na ₂ SO ₄	102·885	1·0498	162·2	2·596	62·5
K ₂ SO ₄	101·392	1·0465	79·4	1·255	63·2
Rb ₂ SO ₄	103·511	1·0513	197·0	2·505	78·6
Cs ₂ SO ₄	109·963	1·0658	545·4	4·015	135·8
Tl ₂ SO ₄	100·317	1·0443	17·8	0·347	51·3
NaNO ₃	120·20	1·0888	1062·9	12·276	86·6
KNO ₃	115·549	1·0786	838·3	12·756	65·7
(RbNO ₃)	119·4	1·0875	1041·0	12·828	81·2)
CsNO ₃	107·228	1·0596	398·1	6·617	60·2
(TlNO ₃)	104·7	1·0541	264·0	11·058	23·9)
Sr(NO ₃) ₂	106·790	1·0587	376·2	3·588	104·8
Cæsium alum	100·527	1·0443	21·2	0·300	70·1

* Porter, *loc. cit.*, p. 523.

The values for the numbers within the brackets are obtained from an earlier communication to the Society,* but the boiling points are not very accurate; we have not yet been able to get satisfactory results with these salts.

It is noticeable that the numbers in the last column for alkali salts which have the same anion seem to increase with increasing molar concentration.

On comparing the numbers in the fourth and fifth columns it will be seen that all the salts, except TiNO_3 , are dissociated. As already mentioned, the results for TiNO_3 are not reliable, but in view of the importance of such an exception we are making further experiments to decide the question.

APPENDIX I.

Solubilities and Densities of Saturated Solutions of Strontium Nitrate.—The densities and solubilities of all the salts dealt with in this communication, except strontium nitrate, were recorded together with the method of work in a previous paper; the following results for the strontium salt were obtained in the manner therein detailed:—

Table VI.

Temperature.	Density.	Weight concentration (number of grammes of anhydrous salt in 100 grammes of water).
° C.		grammes,
0·58	1·28561	40·124
14·71	1·39880	60·867
26·40	1·48831	82·052
29·06	1·51098	87·648
30·28	1·51441	88·577
32·58	1·51408	88·943
39·74	1·51282	90·086
47·73	1·51150	91·446
61·34	1·51048	93·856
68·96	1·51057	95·576
78·98	1·51091	97·865
88·94	1·51174	100·136

These densities and solubilities were plotted against the temperature, and were found to give a transition point of 29·5° C. and 29·4° C. respectively. Mulder (from Landolt and Börnstein) obtained 31·3° and Etard† 32° C. for this point. The discrepancy is so large that it was thought advisable to make some further observations; the results are given below.

A cooling curve of the saturated solution of a sample which had been used

* 'Phil. Trans.' A, 1904, vol. 203.

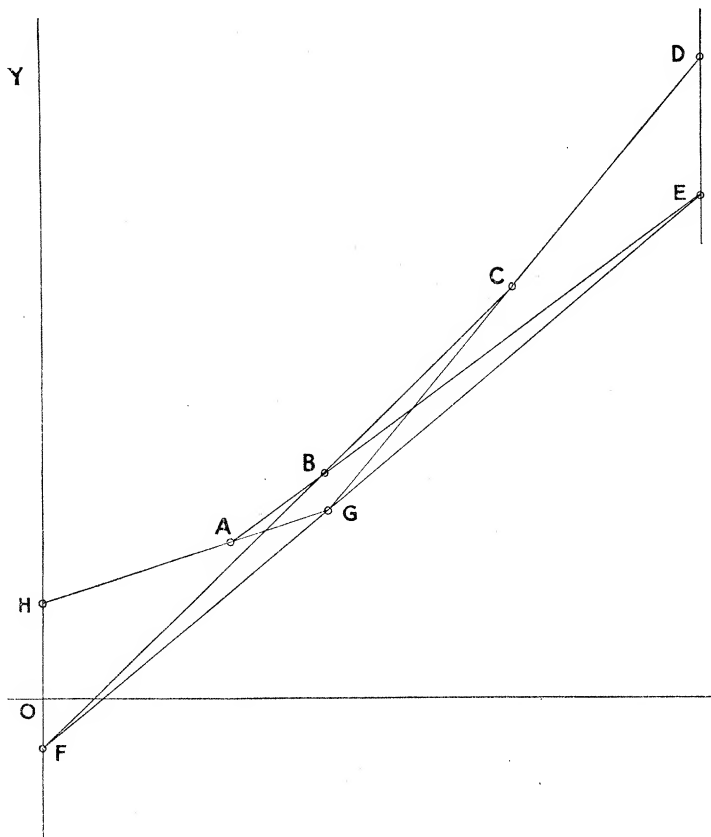
† 'Annales,' [7], vol. 2, p. 528.

for the boiling points gave the transition point as 29.3° , when the super-cooling had been 1.4° . Another similar sample after recrystallisation also gave 29.3° (super-cooling 1°).

An experiment made with a dilatometer, using turpentine as index liquid, gave the transition point as 29.22° .

APPENDIX II.

Given four points A, B, C, and D, on a hyperbola which has an asymptote parallel to the axis OY of reference (see the diagram); required to find the point of intersection between the hyperbola and OY. The points A, B, C, D, and a point I, on the asymptote at infinity, may be regarded as five of the angular points of a hexagon inscribed in the hyperbola; a sixth point is on OY.



By a well-known theorem the points of intersection of the three pairs of opposite sides of a hexagon inscribed in a conic lie on a straight line.

Join AB and produce it to cut ID produced (the ordinate through D) at

E; join BC and produce it to cut the side OY at F; join EF. Join DC and produce it to cut EF in G; join GA and produce it to cut OY in H. It is easy to see that H is the point required.

Pendulum Clocks and their Errors.

By H. R. A. MALLOCK, F.R.S.

(Received May 27,—Read June 29, 1911.)

The measurement of time by pendulum clocks is one of the most accurate measures in daily use, but even with the best existing clocks it is not uncommon to find that the rate may vary from time to time by as much as half a second a day, roughly about 1 part in 150,000.

Clocks are rated by comparison with the rotation of the earth, which is assumed to be constant, and it is a matter of some interest to inquire into the possibility of making a clock good enough to rate the earth by.

The gradual reduction of the angular velocity of the earth as deduced from astronomical data used to be taken as about 22 seconds per century,* but I believe that this estimate is now considered too high.†

At any rate, if a clock is to be accurate enough to give a measure of the change in the earth's angular velocity, it must have a variation of rate not much exceeding one second per century, or about 1 part in 3,000,000,000. It seems hardly possible that this order of accuracy should be reached by any mechanical appliance.

In the following notes, however, I have stated the various causes which may bring about a change in the rate of a pendulum, and the permissible variation of the different arguments involved if the variation of rate due to each of them is not to exceed 1 part in 100,000,000.

The causes of variation of rate may be grouped under three heads, namely :—

- (a) Such as would affect a pendulum swinging freely *in vacuo*.
- (b) Variations due to the action of the atmosphere on a free pendulum.
- (c) Variations due to the action of the mechanism which maintains the vibration.

Of these it will be seen that (c) is the most important and the most

* Thomson and Tait, vol. 1, Part I, p. 400.

† Variation of the length of the day due to contraction by secular cooling would not be indicated by a pendulum clock.